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Effects of Surfactants on the Removal of Carbonaceous Matter and Dioxins from Weathered Incineration Fly Ash

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ABSTRACT

Our previous study demonstrated flotation to be effective in removing carbonaceous matter and dioxins from fresh fly ash in medical waste incinerators (MWIs). However, flotation of weathered fly ash seems to be difficult because of the oxidation of the ash surface and the presence of hydrophilic unburned carbon. Three types of surfactants namely nonionic Tween 80, anionic sodium dodecyl sulfate (SDS) and cationic CTAB were employed at different doses to improve flotation performance. Results indicated that Tween 80 exhibited superior decarburization performance compared with SDS and CTAB. The effect of surfactants on dioxin removal was found to correspond to the carbon removal from MWI fly ash. The optimal removal yields (90.6% of carbonaceous matter and 88.6% of dioxins) were obtained when 5% (w/w) Tween 80 was added. However, an excessive dose might cause the dissolution of dioxins.

Keywords: Weathered fly ash; Flotation; Carbonaceous matter; Dioxins; Surfactant.

INTRODUCTION

Medical waste is regarded as hazardous waste in China because it contains infectious, traumatic, pathological, chemical, and pharmaceutical wastes. Recently, incineration treatment has become the preferred option for waste treatment because of it yields significant volume reduction (approximately 90%) and mass reduction (approximately 70%), as well as a reduction in the toxicity of infectious materials after incineration (Zhan *et al.*, 2016). However, incineration produces a large amount of medical waste incinerator (MWI) fly ash, which is dust-like particles and has high content of chlorine, dioxin and heavy metal. Unburned carbon (UC) is the major source of dioxins in fly ash because of its role in de-novo synthesis and its high adsorption capacity (Huang *et al.*, 2003a; Mallampati *et al.*, 2016). Incineration fly ash has a UC content of approximately 3 wt.% to 10 wt.% (Shibayama *et al.*, 2005). Apart from UC, another type of carbonaceous matter in MWI fly ash is derived from powder activated carbon (PAC) injected into incineration systems as an adsorbent to remove gaseous phase toxic dioxins from the combustion chamber of the flue gas after a series of filtration treatment (i.e., chemical bag filter, electrostatic precipitator, dry/wet scrubber) before dioxins were emitted to the atmosphere (Gao *et al.*, 2010; Liu *et al.*, 2013; Funari *et al.*, 2016; Zhang *et al.*, 2016). Therefore, most of dioxins tend to be absorbed by fly ash in the presence of carbonaceous matter (Shibayama *et al.*, 2005; Chen *et al.*, 2015a). Currently, investigations on the degradation of dioxins in fly ash through thermal degradation, mechanochemical treatment, hydrothermal treatment as well as catalytic hydrodechlorination technique have also been studied. To some extent a reduction of the toxicity of dioxins has been realized (Hu *et al.*, 2015; Weidemann *et al.*, 2015; Wang *et al.*, 2016a; Wang *et al.*, 2016b; Mao *et al.*, 2017). However, most of these techniques may be not suitable for HSWI fly ash treatment due to its special characteristics (Wei *et al.*, 2017a). Consequently, this special type of ash contained with high carbon and dioxin content should be treated with suitable methods.

Flotation has been used for extracting clean coal and separating UC from coal fly ash (CFA) (Qu *et al.*, 2015; Zhou *et al.*, 2017). Since organic compounds such as polychlorinated biphenyls (PCBs), CBs and dioxins are hydrophobic (Wang *et al.*, 2012; Liao *et al.*, 2014; Chen *et al.*, 2014), flotation technology has been also used to remove these organic compounds from municipal solid waste incinerator (MSWI) fly ash (Cheruiyot *et al.*, 2015; Lee *et al.*, 2016; Cheruiyot *et al.*, 2016). Furthermore, organic pollutant removal and UC removal have good linear relationship during flotation of MSWI fly ash (Huang *et al.*, 2007). In our previous work, flotation was employed to separate carbonaceous matter and dioxins from fresh MWI fly ash, and favorable results was obtained (Liu *et al.*, 2013; Liu *et al.*, 2014). A froth product with a combustible matter

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content greater than 50 wt.% of combustible matter could be further treated through reburning in the existing incinerator or microwave oven; thus, dioxins could be effectively decomposed and carbonaceous matter could be reused simultaneously (Wei *et al.*, 2017a, b).

The capacity of ordinary medical waste incineration plants is approximately 10 t d^{-1} in China, and the daily amount of MWI fly ash produced is relatively low (approximately 300–500 kg d^{-1}). In addition, the supply of medical waste and the operation of some incinerators are often batch wise (Chen *et al.*, 2015b). To reduce or prevent secondary pollution during transportation, fly ash is sometimes packed into designated stockpiles within incineration plants for a period of time after the centralized disposal. Storage periods usually range from 3 to 6 months or longer. Such storage under ambient conditions leads to oxidization or weathering of some of the UC surface in the fly ash (Huang *et al.*, 2003a; Dey *et al.*, 2013). The weathering process might decrease the content of hydrophobic groups such as C–H and C–C groups on the coal surface and increase the content of oxygenated functional groups (i.e., hydroxyl, carbonyl, and carboxyl groups) (Xia *et al.*, 2013a, b, 2014; Qu *et al.*, 2015). McCarthy *et al.* (2013) reported the negative effect of the weathering process on carbon recovery from CFA during flotation. Huang *et al.* (2007) pointed out that the existing oxygen contained with functional groups on the surface of UC in MSWI fly ash might reduce the floatability of UC. Thus, the weathering processes make UC more difficult to float with common oily collectors alone. Therefore, it is necessary to seek for some useful methods to enhance the flotation performance (Huang *et al.*, 2003b; Dey *et al.*, 2013b; Xia *et al.*, 2013b).

Two routes, namely pretreatment and surface modification, have been used to eliminate the influence of oxygen-containing functional groups and to improve the hydrophobicity of oxidized coal or UC (Huang *et al.*, 2003b; Dey *et al.*, 2013; Qu *et al.*, 2015). The typical methods for treating oxidized coals include thermal treatment, microwave disposal, premixing or preconditioning, and grinding (Xia *et al.*, 2013a; Dey *et al.*, 2013). These methods facilitate absorption of carbon by collectors or reduction of the oxygen-containing functional groups on the coal surface. In addition, surface modification with appropriate surfactants can enhance the flotation performance by improving the hydrophobicity of particles' surfaces (Dey *et al.*, 2013; Feng *et al.*, 2013). The synergistic effect of surfactants on flotation has also been studied. Zouboulis found that addition of a surfactant was necessary for effective separation of PAC from suspension (Zouboulis *et al.*, 1994; Lu *et al.*, 2013). In addition, Huang *et al.* (2003b) demonstrated that added surfactants could facilitate the removal of organic compounds and UC from weathered MSWI fly ash.

Researchers have tested numerous surfactants to determine which ones improve the flotation separation efficiency (Zhou *et al.*, 2017). They have found that the effects of surfactants on the flotation performance mainly depend on surfactant types and doses (Wang *et al.*, 2013). Cationic, anionic and nonionic surfactants are the most commonly employed surface modification regents in flotation. Vamvuka *et al.* (2001) reported that the overall performance for cationic surfactants was superior to that of anionic and nonionic ones during the flotation of lignite. Mouton *et al.* (2009) demonstrated that the performance of nonionic surfactants in polycyclic aromatic hydrocarbon (PAH) removal was superior to that of amphoteric ones. Qu *et al.* (2015) reported that nonionic 2-ethyl hexanol provided better flotation performance during flotation of low-rank coal than cationic DDA or anionic SDS. Zhou *et al.* (2017) demonstrated that nonionic surfactants had stronger synergistic ability than anionic surfactants during the flotation of CFA. In addition, the surfactant doses also affect the flotation effects. Zouboulis *et al.* (1994) proved that cationic CTMA-Br was a more effective surfactant for PAC flotation than SDS at relatively small doses (100 mg L^{-1}).

Previous investigations have demonstrated that the feasibility of using surfactants for removing UC and organic compounds such as PCBs, CBzs and dioxins from weathered MSWI ash (Huang *et al.*, 2003a, b, 2007). These studies have examined UC in MSWI fly ash but have not addressed PAC. MWI fly ash contains a mixture of UC and PAC which has a high adsorption capacity and might affect dioxin partition during flotation. However, little research has addressed the effect of the surfactant types (cationic, non-ionic and anionic surfactants) on the flotation behavior of weathered MWI fly ash. Therefore, tests were performed to investigate the effect of the surfactant types and doses on the flotation performance of MWI fly ash. In addition, surface tension was also tested to provide further information on carbon removal.

MATERIALS AND METHODS

Materials

The sample ash was collected from fabric filter devices stored at dump site in incineration plants in southern China, which are equipped with 15 t d^{-1} gyration kiln incinerator. The sample ash was subjected to weathering for 6 months. Then it was homogenized and screened by a sieve of 20 meshes to remove large particles, and dried at 105°C for 24 h. The loss on ignition (LOI) of the sample was determined in accordance with the standard for pollution control (GB18485-2014). The ash sample containing a large amount of PAC was derived from PAC sprayer device, and its LOI was 15.8% (on dry basis). Major compounds and heavy metals in MWI fly ash was showed as Table 1.

Flotation Methods

Flotation tests were performed in a 1 L Denver flotation cell (RK/FD111 type). In preliminary research, the operating parameters of flotation were first examined on the basis of a previous flotation experiment (Liu *et al.*, 2013). The optimal parameters adopted in this experiment were 100 g L^{-1} of slurry concentration, 3.0 g kg·ash^{-1} of kerosene dose, 0.1 g kg·ash^{-1} of MIBC, 1.2 L min^{-1} of air flow rate and 2000 rpm of impeller speed. The kerosene collector, MIBC and certain doses of surfactants at certain doses were added into the slurry one by one, and the conditioning time for these reagents was 3 min, 2 min and 1 min, respectively. After

Table 1. Major compounds and heavy metals in MWI fly ash.

Major compounds	Mass fraction (%)	Heavy metals	Content (mg kg^{-1})
SiO_2	14.31	Pb	2232
CaO	23.55	Zn	8507
Al_2O_3	3.65	Cu	794
Fe_2O_3	3.31	Cd	146
MgO	1.09	Cr	124
K_2O	4.58		
Na_2O	17.03		
SO_3	4.83		
Cl	22.38		
TiO_2	0.99		
F	1.19		
LOI	15.84		

conditioning for appropriate times, the slurry was transferred into a flotation cell and flotation was performed. In this process, deionized water was continuously added into the cell to maintain a constant pulp level. The froth product was collected and manually separated from top of the cell during flotation period (impeller rotation speed = 2000 rpm, flow rate = 1.2 L min^{-1}). To achieve the desired separation performance, a two-stage flotation process was applied as described in our previous study (Liu *et al.*, 2013). After the flotation test, the froths and the tailings were filtered, dried, weighed and analyzed for both dioxins and carbon.

In this study, three types of surfactants (i.e., nonionicTween80, cationic CTAB and anionic SDS) were used as promoters to improve the floatability of the weathered fly ash (Table 2). The surfactant doses were ranged from 2.5 wt.% to 10 wt.% of the kerosene doses. To facilitate comparison, other operating conditions were kept the same and the pH value of the original slurry was adjusted to 7.

The concentrations of PCDD/F and its congeners (2,3,7,8-substituted) were analyzed using the isotope dilution high resolution gas chromatography-high resolution mass spectrometry. And the dioxin analytic method was described in detail in our previous study (Wei *et al.*, 2016a). TEQs of dioxin congeners in the sample were calculated on the basis of international toxic equivalency factors.

Furthermore, to elucidate the flotation results, surface tension experiments were conducted on 100 mL of slurry as described for the flotation tests. The surface tension was measured using Dataphysics DCAT21 coupled with the Wilhelmy plate method at room temperature.

RESULTS AND DISCUSSION

Effects of Surfactant Type and Dose on Decarburization Performance

The decarburization effects of surfactant type and addition dose were investigated by adding Tween 80, CTAB and SDS. The results are presented in Fig. 1. Weight loss reached 64.4% owing to a large amount of chloride dissolution, which was significantly higher than that of MSWI fly ash during flotation (6–7%) (Shibayama *et al.*, 2005). Carbon removal efficiency was only 73.4% when no surfactant was added. It sharply increased after Tween 80 was added and reached a maximum when the Tween 80 dose was 5%. Similar trends were obtained with the addition of CTAB and SDS. The highest efficiencies of carbon matter removal were 90.6%, 83.2% and 82.1% for Tween 80, CTAB and SDS, respectively, meanwhile, and the LOI of the tailings decreased to minimums of 5.7%, 10.4%, and 11.7%, respectively. These results indicate that Tween 80 is more effective for carbon removal than CTAB and SDS at the same doses. The effects of the surfactant type on carbon removal was approximately consistent with the work of Zhou *et al.* (2017), who concluded that the effect of nonionic Tween 80 was superior to that of anionic SDS during combustible recovery from CFA.

The addition of anionic SDS did not significantly increase the efficiencies of carbonaceous matter removal. This is because of the nonselective adsorption of anionic SDS on both the mineral matter and the surface of carbonaceous matter (Qu *et al.*, 2015). In addition, although hydrogen bonding occurred between polar anionic SDS and the carbon surface, electrostatic repulsion between negatively charged surface of UC and the anionic SDS decreased the probability of adhesion between carbon particles and collectors (Zhou *et al.*, 2017). Cationic CTAB was certified to carry the opposite charge with negatively charged surface of UC, and the oily collector possibly interacted with the UC surface through electrostatic attraction and hydrogen bonding (Qu *et al.*, 2015). It seems logical that the flotation effect of UC in the presence of cationic CTAB was slightly higher than that of SDS from an electrostatic perspective. However, as for the flotation effect of PAC, cationic CTAB might have few differences from SDS. This might be because the PAC surface can adsorb molecules with positive or negative charges, and thus both cationic and anionic surfactants could effectively float PAC (Zouboulis *et al.*, 1994).

This synergistic effect of nonionic Tween 80 on the carbon removal efficiency during flotation may be attributed to two interaction mechanisms for UC and PAC. Regarding the chemical structure, nonionic Tween 80 is bifunctional and possesses oxygenated functional groups, namely carboxyl and hydroxyl; sorbitol esters and hydrocarbon chains (Huang *et al.*, 2007). After weathering of MWI fly ash, the surface of UC contains a large number of oxygen-containing functional groups such as carboxylic (–COOH)

Table 2. Characteristics of used surfactants

Surfactant	Structural formula	Critical micelle concentration (mol L^{-1})	Hydrophilic–lipophilic balance	Type
Tween 80	$C_{64}H_{124}O_{27}$	1.2×10^{-5}	15.0	Non-ionic
CTAB	$C_{19}H_{42}BrN$	9.2×10^{-4}	15.8	Cationic
SDS	$C_{12}H_{25}SO_4Na$	8.3×10^{-3}	13	Anionic

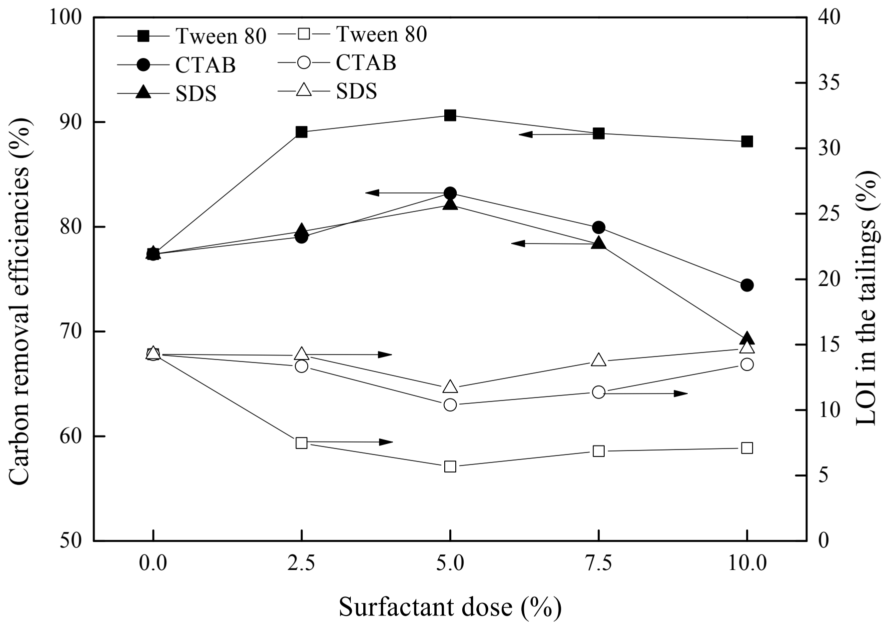

Fig. 1. Effect of surfactant type and dose on carbon removal efficiencies and LOI in the tailings.

ester and phenolic (OH) groups. The polar oxygenated functional groups of nonionic Tween 80 might interact with the oxygenated functional groups on the UC particle surface. Furthermore, the nonpolar aliphatic chain of nonionic Tween 80 might interact with PAC through hydrophobic bonding (van der Waals interaction) (Huang *et al.*, 2003b, 2007; Qu *et al.*, 2015). In addition, the nonionic surfactant could emulsify the kerosene and increase the number of oil droplets. Then the UC and PAC particle surface would be firmly attached by kerosene after emulsification (Huang *et al.*, 2003a). Furthermore, the surfactants with a high hydrophilic-lipophilic balance (HLB) value have more oxygenated functional groups and are more conducive to removal of UC from MWI fly ash. Huang *et al.* (2007) concluded that the optimum HLB value is 13.5 for a mixture of two types of nonionic surfactants. In addition, the tail length of the surfactants influences adsorption of kerosene and the flotation effect (Zhou *et al.*, 2017).

Fig. 1 illustrates that all three types of surfactants in this study yielded maximum carbon removal efficiencies at the same dose of 5% w/w (surfactant/collector). These results generally agree with the investigation of Zouboulis *et al.* (1994), who concluded that the optimum dose of cationic CTMA-Br and anionic SDS were similar in PAC removal. Huang *et al.* (2003b) indicated that the optimum surfactant dose was 3% in kerosene for the removal of UC from MSWI fly ash through flotation. It is generally believed that the initial adsorption of surfactants occurs with the polar groups orientated toward the solid surface. If the surfactant dose exceeds the optimum value, the excess hydrophilic part of the surfactants would lead to a reduction in the hydrophobicity of the carbon particle surface and thus decrease the removal efficiency of carbonaceous matter (Zouboulis *et al.*, 1994; Huang *et al.*, 2003b, 2007; Qu *et al.*, 2015).

Effects of Surfactant Type on Surface Tension of Slurry

Surface tension is a crucial parameter for assessing the flotation performance since the flotation process is based on the surface properties of mineral particles. The surface tension of slurries with or without the addition of surfactants is shown in Fig. 2. The slurry without surfactants had a surface tension of 75.8 mN m^{-1}, which is higher than that of deionized water (72.8 mN m^{-1}) (Qu *et al.*, 2014). Reduction of the surface tension of the slurry was observed in the presence of surfactants, which agrees with the results of Sis *et al.* (2003). The three types of surfactants are ordered according to surface tension as follows: Tween 80 < CTAB < SDS. This order is inconsistent with the results of Qu *et al.* (2014). Zhou *et al.* (2017) reported that the reduction of surface tension values for Tween 80 was approximately 2 times that for SDS. In this study, differences between the types of surfactants were small, which is inconsistent with the results reported by Qu *et al.* (2014) and Zhou *et al.* (2017). This might be because the high salt concentration in the slurry was attributable to the dissolution of chlorides in MWI fly ash, which increased the surface tension of the aqueous solution (Ozdemir *et al.*, 2011). The lowest surface

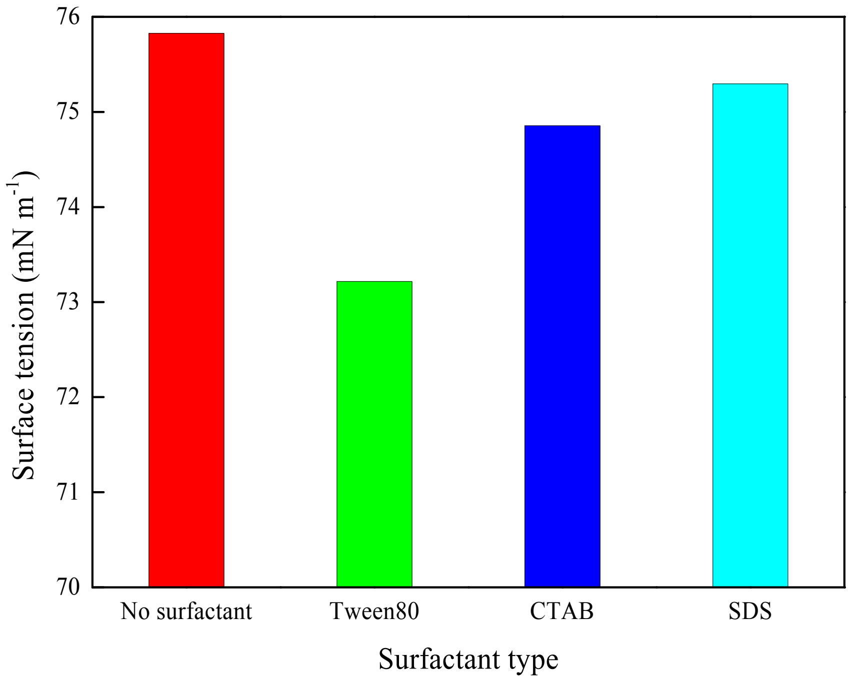

Fig. 2. Effect of surfactant type on surface tension of the slurry (5% (w/w) of dose).

tension of surfactants might be beneficial for the improvement of bubble adhesion and the spreading of the oily collector (Qu *et al.*, 2014). Tween 80 provides the highest reduction of surface tension and may be more readily adsorbed on the UC surface, which can further improve performance in decarburization flotation.

Effects of Surfactant Type and Dose on Dioxin Removal

The influence of the surfactant type on dioxin removal at the same surfactant dose is shown in Fig. 3. Adding a surfactant significantly improves the dioxin removal in comparison flotation without a surfactant. After the application of Tween 80, SDS and CTAB, the total dioxin removal efficiencies were 88.6%, 81.0% and 81.9%, respectively. These results indicated that Tween 80 was more efficient than the other two surfactants, which may be attributed to its high carbon removal efficiency.

The flotation removal mechanism of dioxins from MWI fly ash is complex. Furthermore, sorptive-flotation should be taken into consideration because of the presence of PAC in the slurry (Fig. 4). An explanation for the dioxin removal mechanism may be on the basis of the porous structure of PAC. PAC is a unique and versatile adsorbents because of its large surface area, micro-porous structure, and high adsorption capacity (Wang *et al.*, 2004). A proportion of dioxins might be shed from solid ash particles and enter to the aqueous phase during flotation, and substantial proportions of these dioxins might be arrested and adsorbed onto PAC. In addition, there is initially a close adsorption relationship between the gaseous phase dioxins and PAC/UC in fly ash (Nagano *et al.*, 2000), and this affinity persists in the flotation process. Thus, these adsorbed dioxins might be readily removed from the froths together with PAC through a combination of adsorption and flotation. Fly ash has a high content of PAC, which seems to have a significantly high potential to adsorb dioxins and cause upward transportation of dioxins (Yasuhara *et al.*, 2007). Consequently, sorptive-flotation is likely to be a dominating process in dioxin removal (Ghazy *et al.*, 2006). In addition, a small proportion of dioxins may directly attach to kerosene collectors or directly adhere to the air bubbles, and finally float to the froth product.

Tween 80 has proved to be an effective surfactant for carbon and dioxin removal according to Fig. 3 and the previously described results. Furthermore, dioxin removal efficiency mainly depends on the surfactant dose. The influence of Tween 80 dose on dioxin removal is shown in Fig. 5. The efficiency of dioxin removal from the froths increased initially with an increasing Tween 80 dose. And the maximum removal efficiencies for both dioxins and carbon were achieved at the surfactant dose of 5 wt.%, and dioxin removal had a trend similar to that of carbon removal. The highest dioxin removal efficiency (88.6%) is far higher than the value 41.9% from MSW fly ash reported by Huang *et al.* (2007), which might be related the different characteristics of two types of fly ash such as the content of PAC, particle size and form of dioxins. A suitable particle size distribution has positive effect on the removal efficiency. The particle size range of < 106 µm is optimum for froth flotation, and the value of MWI fly ash (98%) is higher than that of MSWI fly ash (46%–59%), which benefit both carbon removal and dioxin removal (Huang *et al.*, 2003c; Wei *et al.*, 2016). In addition, almost all PAC can be removed from dilute aqueous suspensions as long as suitable flotation conditions are available (Zouboulis *et al.*, 1994). Furthermore, PAC may have a larger adsorption capacity to retain dioxins, which results in higher dioxin removal efficiency (Yasuhara *et al.*, 2007).

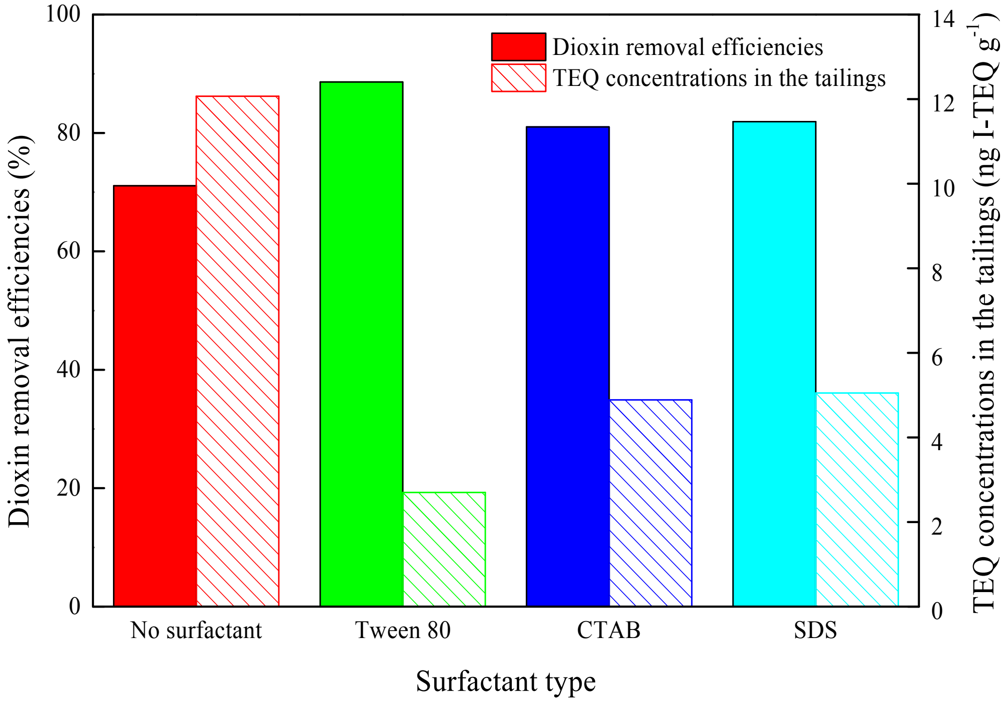

Fig. 3. Effect of surfactant type on dioxin removal efficiencies and TEQ concentrations in the tailings.

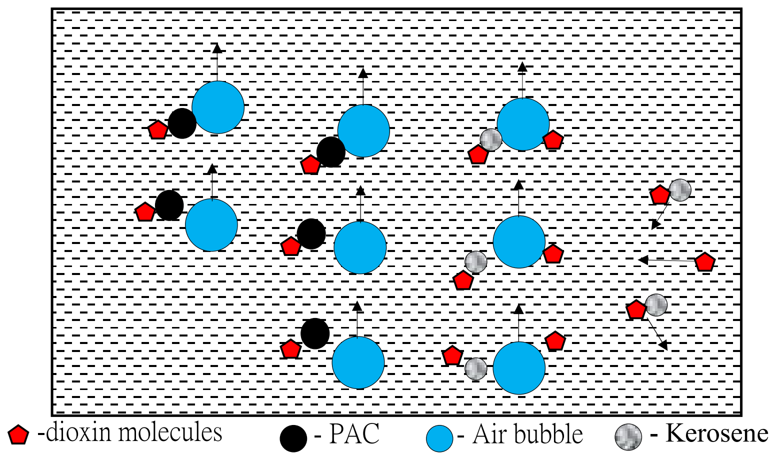

Fig. 4. Conceptual diagram of the dioxin removal by sorptive-flotation.

Effects of Surfactant Dose on Leaching Ratio of Dioxins

The leaching ratio is defined as the partition ratio of dioxins remaining in the aqueous phase slurry after flotation of fly ash. Fig. 6 shows the leaching ratios at various doses of Tween 80. The ratios of dioxins dissolved in the aqueous phase are much lower than those in the froths and the tailings. In the absence of surfactants, the leaching ratio was only 0.37%, which is similar to levels observed in various types of MSWI fly ash (Huang *et al.*, 2007; Yasuhara *et al.*, 2007). Dioxins, as hydrophobic organic pollutants (HOPs), are not easily soluble in water but are easily attached to solid particles.Even when pure water is used as the elution solvent for dioxin leaching, the amount of dioxins eluted into water is very low (Yasuhara *et al.*, 2007).

However, the leaching ratios of dioxins increased obviously with an increase of the Tween 80 dose. The value reached 7.47% at the highest surfactant dose of 10%. A surfactant can be used not only as an effective activator agent for the flotation of carbonaceous matter, but also to enhance the dissolution of organic contaminants in soils (Dermont *et al.*, 2008). Despite the low water solubility of dioxins, the surfactants could enhance the solubility of dioxins in fly ash (His *et al.*, 2008). A synergistic effect of surfactants on the solubility of HOPs has been revealed. Yasuhara *et al.* (2007) pointed out that the quantity of dioxins eluted from fly ash by non-ionic surfactant solution was extremely high because of the relatively high solubility of dioxins in the solvent. In addition, Huang found that the leaching ratio reached 3.2% when using a non-ionic surfactant in the flotation of MSWI fly ash but the value was only 0.04% without surfactant addition. He attributed this mainly to the surfactant enhancing the strong connections

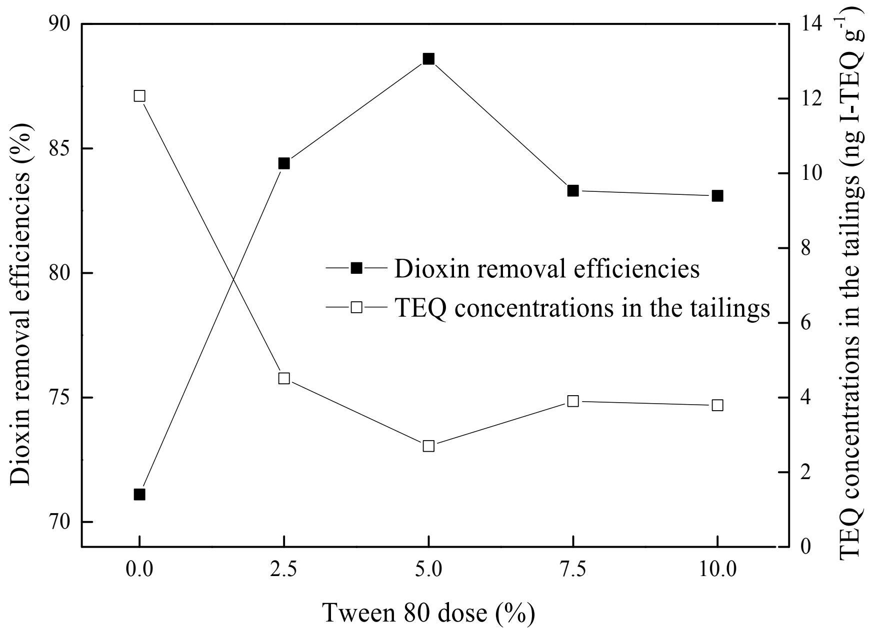

Fig. 5. Effect of Tween 80 dose on dioxin removal efficiencies and TEQ concentrations in the tailings.

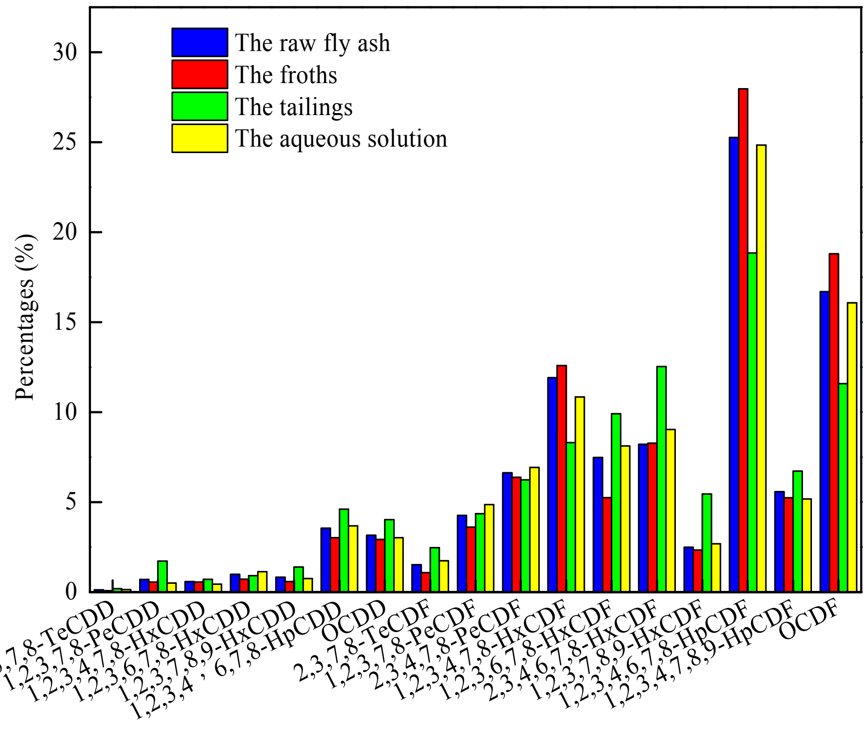

Fig. 6. Percentage distribution of 17 major PCDD/F congeners in raw fly ash and flotation products.

between the UC and the kerosene which resulted in the dissolution of more dioxins in the kerosene and then in the aqueous phase (Huang *et al.*, 2007). Although addition of surfactants could be efficient in removing carbon and dioxins, an excessive surfactant dose may pose problems owing to the surfactant-enhanced solubilization (Wang *et al.*, 2004). Sorption sites in PAC may be saturated due to the dissolution of a large amount of other organic pollutants such as chlorobenzenes, PAHs, PCBs from fly ash, and the reduction effect of sorptive-flotation of dioxins. Hence, the dissolved dioxins cannot be completely adsorbed by PAC owing to a lower PAC load, and hence, the rest of them remain in the aqueous phase slurry (Wang *et al.*, 2008).

Dioxin Congener Distribution before and after Flotation

Fig. 6 shows the percentage distribution of 17 major dioxin congeners in raw fly ash and flotation products at a 5% (w/w) dose of Tween 80. Among all toxic congeners in raw fly ash, 1,2,3,4,6,7,8-HpCDF (25.3%) and OCDF (16.7%) were more predominant, and the percentages of PCDF congener constituents were higher than those of PCDD compounds, which may be related to the high chlorine content in the feed material of the MWI. When the chlorine content exceeded the threshold (0.8%–.1%), the rate of PCDF formation also exceeded that of PCDDs (Wang *et al.*, 2003). In addition, the higher PCDF concentrations than the PCDD concentrations suggested that de- novo synthesis reactions were the primary mechanism of dioxin formation at the plant (Gunes *et al.*, 2015).

Since the dioxins were separated from fly ash, the dioxin congener profiles in the flotation products (the froths, the tailings and aqueous phase) were similar to that of fly ash. The concentrations of high chlorinated congeners in the froths were higher than those of low chlorinated congeners. Furthermore, the proportions of 1,2,3,4,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDD and OCDD in the froths were higher than those in the raw fly ash. This might be due to their relatively high initial concentrations in PCDD/Fs. Owing to flotation, the residual concentrations of dioxins retained a similar low level and dioxins with higher initial concentrations seemed to have higher removal efficiencies (Zhou *et al.*, 2016). Flotation cannot alter the congener fingerprint of dioxins in the aqueous phase significantly. Accordingly, Zhou *et al.* (2016) found that the fingerprint of dioxins contained in an n-hexane solution was similar to that of fly ash.

Dioxin Partition in Final Products after Flotation

Flotation causes the partition of dioxins among three products namely the froths, the tailings and aqueous phase. Under the optimum flotation conditions (5% (w/w) Tween 80), the total dioxin concentration in the froth product reached 444.5 ng g^{-1}. The amount of dioxins in the froths is approximately 4-fold higher than that in fly ash. These dioxins are decomposed during subsequent reburning or microwave treatment of the froths. The total dioxin concentration was decreased from 89.9 ng g^{-1} in the fly ash to 30.8 ng g^{-1} in the tailings. At the same time, the TEQ concentration decreased from 7.0 ng I-TEQ g^{-1} to 2.7 ng I-TEQ g^{-1} in the tailings, the values in the tailings meet the landfill regulation requirements (< 3 ng I-TEQ g^{-1}). Therefore, the tailings could be directly disposed in landfills without further treatment of dioxins, thereby serving the two-fold aim of dioxin removal and tailing disposal. During flotation process, the increase in dioxin leachability owing to the addition of surfactants may have a negative impact on the environment. Dioxins in the aqueous phase of the slurry must be degraded through techniques such as catalytic degradation and photodegradation before being disposed of in order to avoid further environmental pollution (Huang *et al.*, 2007; Cobo *et al.*, 2009). To avoid the leaching of dioxins, the flotation of weathered fly ash can be improved through pretreatment methods such as thermal treatment, microwave treatment, premixing or preconditioning, and grinding, without the addition of surfactants. Further work is necessary to investigate the effect of pretreatment of weathered fly ash on the improvement of flotation.

CONCLUSIONS

This paper presents a comparison of the performance of Tween 80, SDS and CTAB surfactants for the removal of carbonaceous matter and dioxins from weathered incineration fly ash through flotation. Results showed that the flotation of the weathered fly ash without adding surfactants was ineffective. The surfactants are ranked as follows according to their synergistic effect on the removal of carbon constituents from fly ash through flotation: Tween 80 > CTAB > SDS > no addition. 90.6% of carbonaceous matter and 88.6% of dioxins could be removed from the weathered fly ash when 5% (w/w) Tween 80 was added. Leaching ratios of the dioxins obviously increased with an increase in surfactant dose. The congener profiles of dioxins in flotation products and fly ash were similar. Under the optimal conditions, the residual dioxins in the tailings meet the landfill regulation requirements.

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